

Silver ion enhanced C-H activation in Pt(II) hydroxo complexes.

Tracy L. Lohr, Warren E. Piers* and Masood Parvez

*Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta,
Canada T2N 1N4.*

E-mail: wpiers@ucalgary.ca

Supporting Information

General Experimental Details	S2
Figure S1. Concentration vs Time plot for 3-Ag to 4-Ag	S3
Figure S2. Concentration vs Time plots for 2-Ag to 4-Ag (wet vs dry)	S4
Figure S3. Concentration vs Time plot for 2 at 308 K (with 2-Ag)	S4
Figure S4. ¹ H NMR spectrum of 1-Ag	S5
Figure S5. ¹³ C DEPT-Q NMR spectrum of 1-Ag	S5
Figure S6. ¹ H NMR spectrum of 2-Ag	S6
Figure S7. ¹³ C DEPT-Q NMR spectrum of 2-Ag	S6
Figure S8. ¹⁹⁵ Pt NMR spectrum of 2-Ag	S7
Figure S9. ¹ H NMR spectrum of 3-Ag	S7
Figure S10. ¹³ C DEPT-Q NMR spectrum of 3-Ag	S8
Figure S11. ¹⁹⁵ Pt NMR spectrum of 3-Ag	S8
Figure S12. Stacked IR spectra of 1-Ag , 2-Ag , and 3-Ag	S9
Table 1. Data table and refinement parameters for 1-Ag	S10
References	S10

General considerations.

An argon filled glove box was employed for manipulation and storage of all oxygen and moisture sensitive compounds. All reactions were performed on a double manifold high vacuum line using standard techniques.¹ Residual oxygen and moisture were removed from the argon stream by passage through an OxisorBW scrubber from Matheson Gas Products. Toluene, tetrahydrofuran, and hexanes solvents were dried and purified using the Grubbs/Dow purification system² and stored in evacuated 500 mL bombs over sodium- tetraglyme/benzophenone ketyl. Pentane and dichloromethane were dried, distilled, and stored in an evacuated 500 mL bombs over sodium-tetraglyme/benzophenone ketyl (pentane) and calcium hydride (dichloromethane). All solvents were distilled prior to use. Water and deuterium oxide were degassed by 3 freeze-pump-thaw cycles and stored in a glovebox designated for water usage, or in a sealed glass bomb. *d*₅-bromobenzene and *d*₆-benzene were dried over and distilled from CaH₂, and were stored in glass bombs in a glove box. Solutions of 30 mMol/L H₂O in C₆D₆ were made up in volumetric glassware in a glovebox designated for water usage and stored in a sealed glass bomb or in a sealed vial in the glovebox freezer at -35°C. ¹⁹⁵Pt NMR spectra were run on a CFI-600 spectrometer and referenced to K₂PtCl₄ in D₂O. ¹H, and ¹³C chemical shifts were referenced to residual proton, and naturally abundant ¹³C resonance of the deuterated solvent, respectively. Assignments of chemical shifts are based on ¹H, ²H, ¹³C, DQF-COSY, ¹H,¹³C-HMQC, and NOESY NMR spectra performed on Bruker RDQ-400, DRY-400, UGI-400 and CFI-600 spectrometers. Multi-day room and high temperature ¹H NMR cycling experiments were performed on a CFI-600 spectrometer. NMR spectra were processed and analyzed with MestReNova (v7.0.2-8636). High-resolution mass spectra were obtained using a Bruker Esquire 3000 spectrometer operating in electrospray ionization (ESI) mode. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on a Nonius KappaCCD diffractometer by Dr. Masood Parvez of this department; full details can be found in the independently deposited crystallography information files (cif). Elemental analyses were performed using a Perkin-Elmer model 2400 series II analyzer by Johnson Li of this

department. Silver(I) oxide and Silver bis-(N-trifluoromethanesulfonyl)imide were purchased from Aldrich and used as received and stored in the glovebox. Hexamethylbenzene was purchased from Eastman Organic Chemicals, sublimed at 70°C under static vacuum and stored under argon. All NMR solvents were purchased from Cambridge Isotope Laboratories Inc. and Sigma Aldrich and dried according to the procedures outlined above or used as received. All air-sensitive compounds were stored in the glove box. Compounds 1,³ 2,⁴ 3,⁵ and 4⁴ have been previously reported. All IR spectra were done as a THF film sandwiched between two NaCl plates and sealed from air in the glovebox by sealing the outer edges of the plates with black electrical tape.

¹⁹⁵Pt NMR data for previously reported complexes:

1 (107 MHz, THF-d₈, 298K): -547 ppm.

2 (107 MHz, C₆D₅Br, 298K): - 1485 ppm.

3 (107 MHz, C₆D₅Br, 298K): - 1272 ppm.

4 (107 MHz, C₆D₆, 298K): - 2656 ppm.

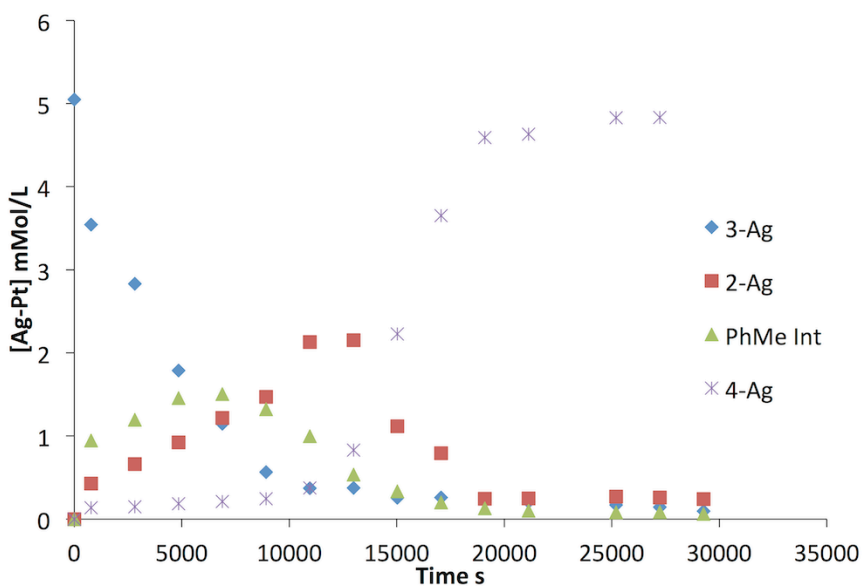


Figure S1. Concentration versus time plot for the conversion of **3-Ag** to **4-Ag** at 328K in C₆D₆ (30 mMol/L H₂O). Starting [**3-Ag**] 5.05 mMol/L. Two intermediates were observed, one which matched the spectroscopic features of **2-Ag** with elimination of

CH₃D, and a new species which we tentatively assigned as the silver associated complex (NN)Pt(CH₃)(C₆D₅)-Ag.

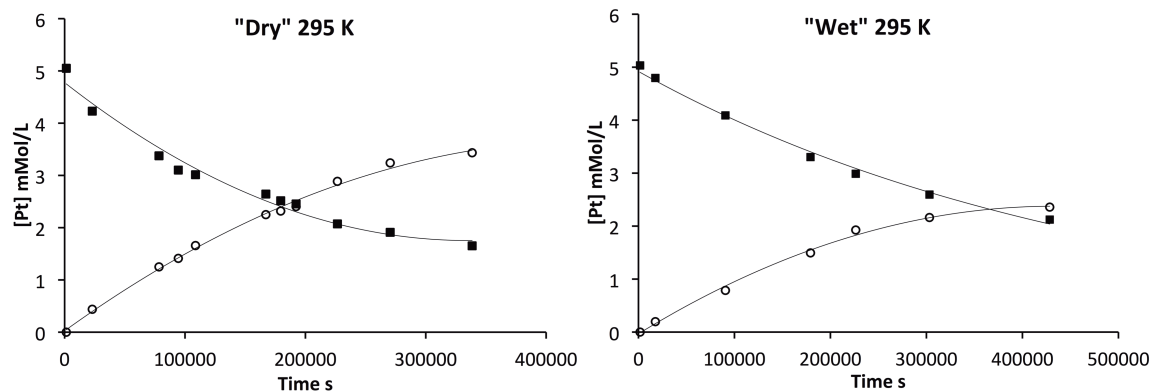


Figure S2. Concentration versus time plots for the conversion of **2-Ag** to **4-Ag** at 295 K in dry C₆D₆ (left) and wet C₆D₆ (30 mM H₂O, right). Squares: **2-Ag**, open circles: **4-Ag**. The reaction does go to completion but was not followed further and stopped after ~ 5 days. Each run at 295 K (wet and dry) was performed in triplicate.

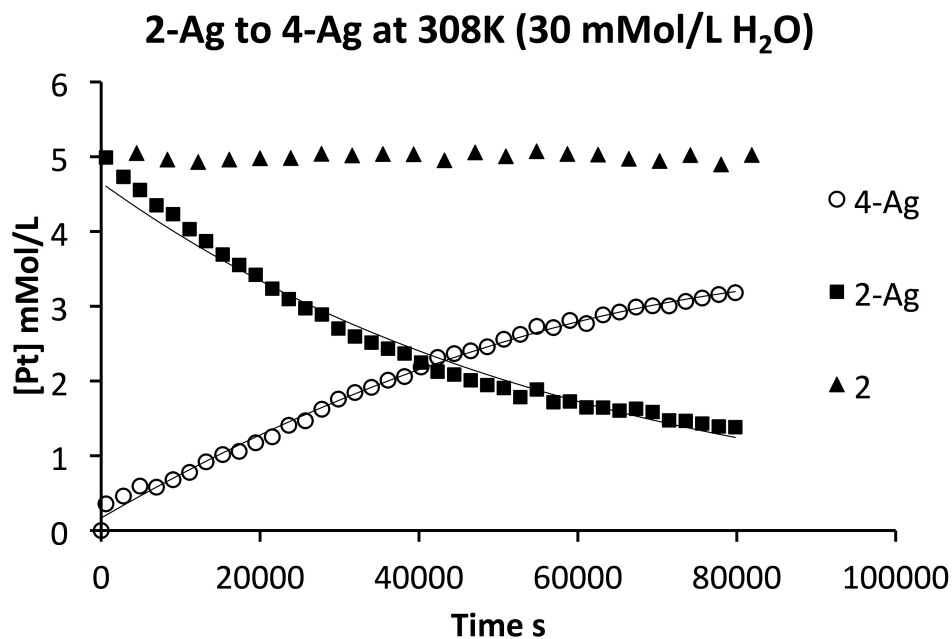


Figure S3. Concentration versus time plots for the consumption of **2-Ag** (squares) to **4-Ag** (open circles) at 308 K overlaid with a plot of **2** (triangles) at 308 K.

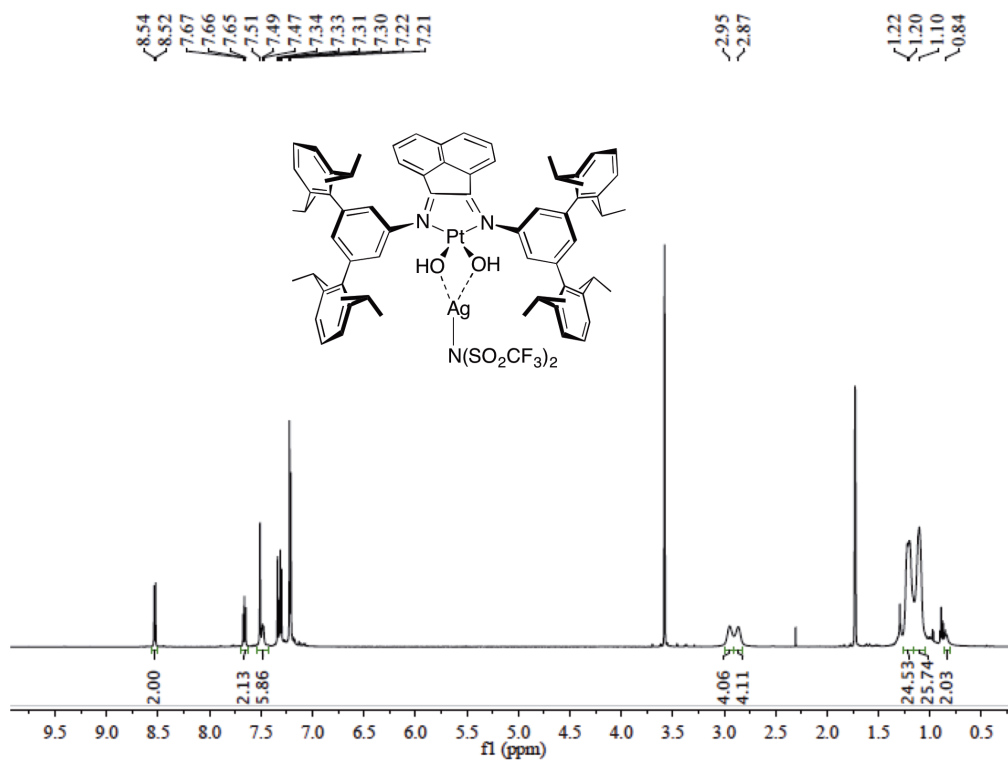


Figure S4. ^1H NMR of 1-Ag in THF- d_8

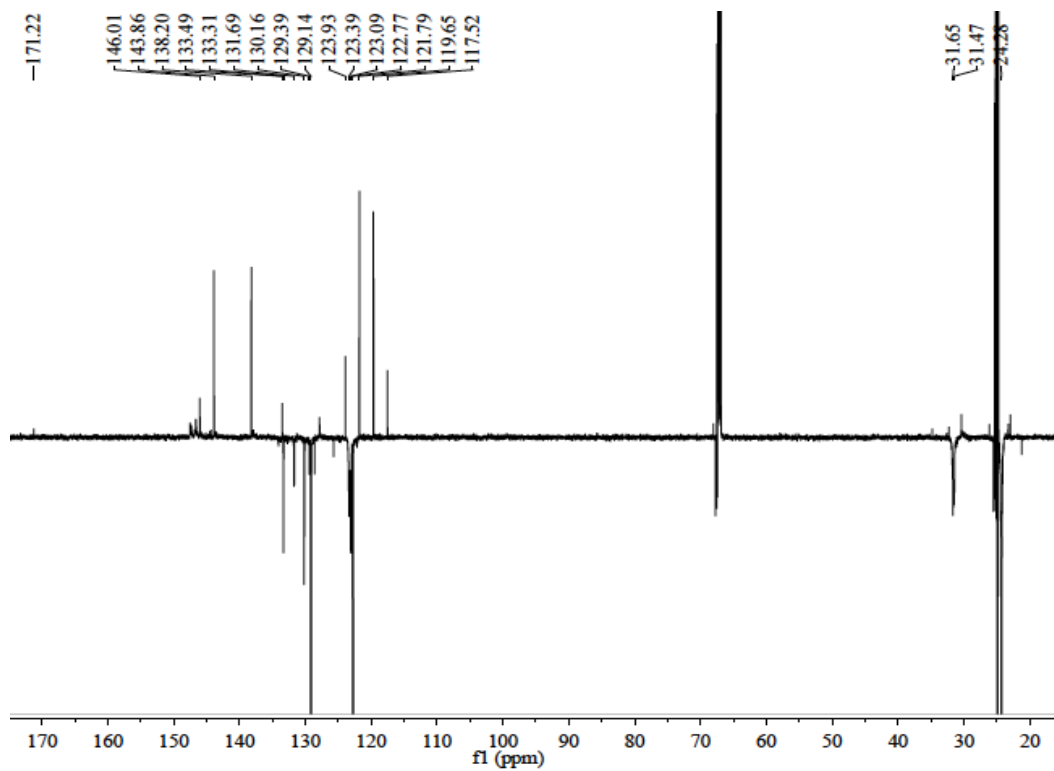


Figure S5. DEPT-Q ^{13}C NMR of 1-Ag in THF- d_8 at 298K

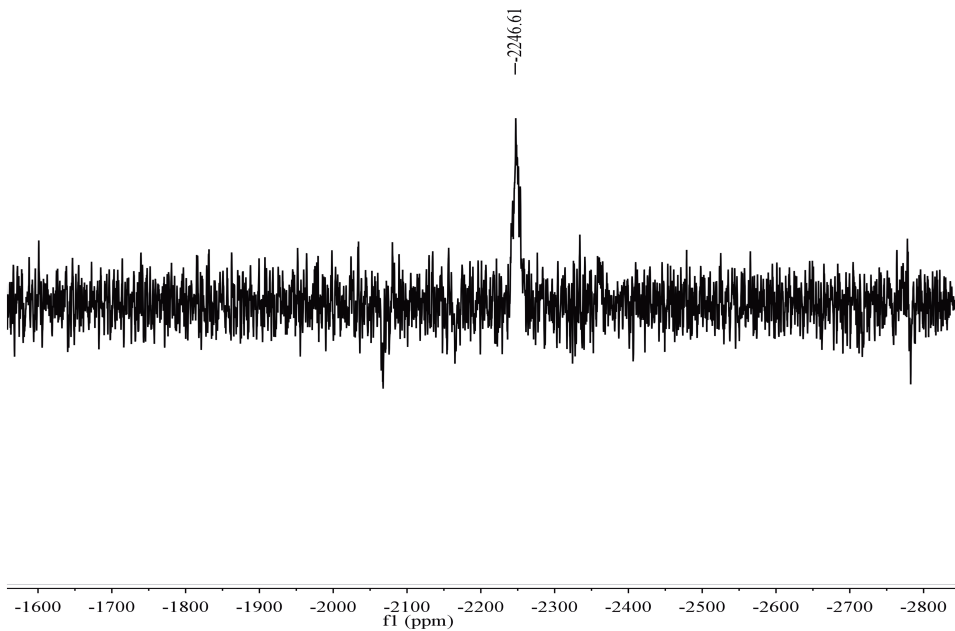


Figure S8. ^{195}Pt NMR of **2-Ag** in $\text{C}_6\text{D}_5\text{Br}$ at 298K

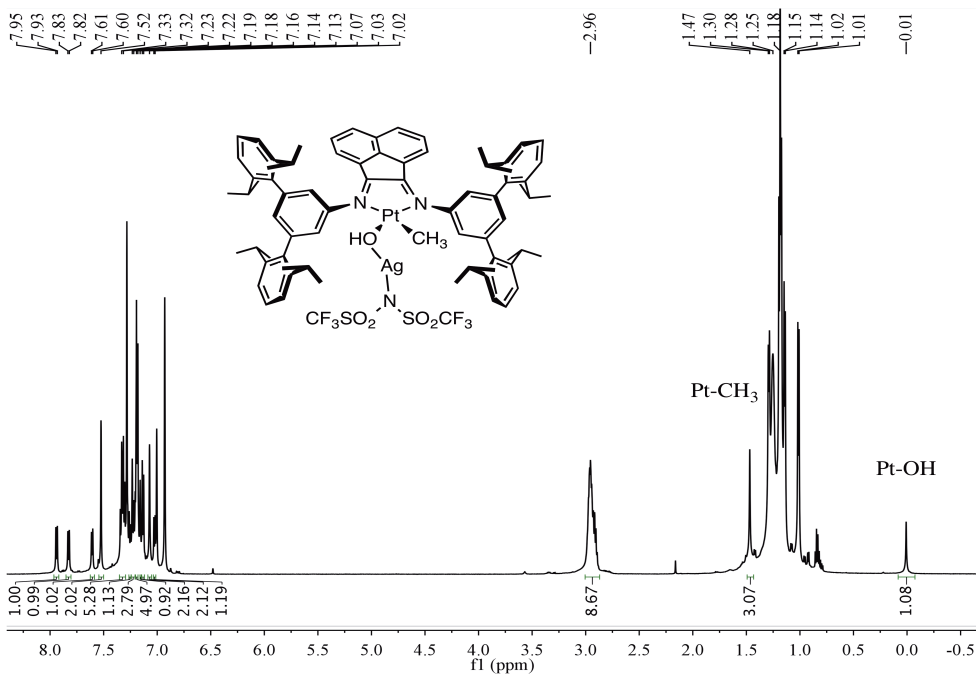


Figure S9. ^1H NMR of **3-Ag** in $\text{C}_6\text{D}_5\text{Br}$ at 298K

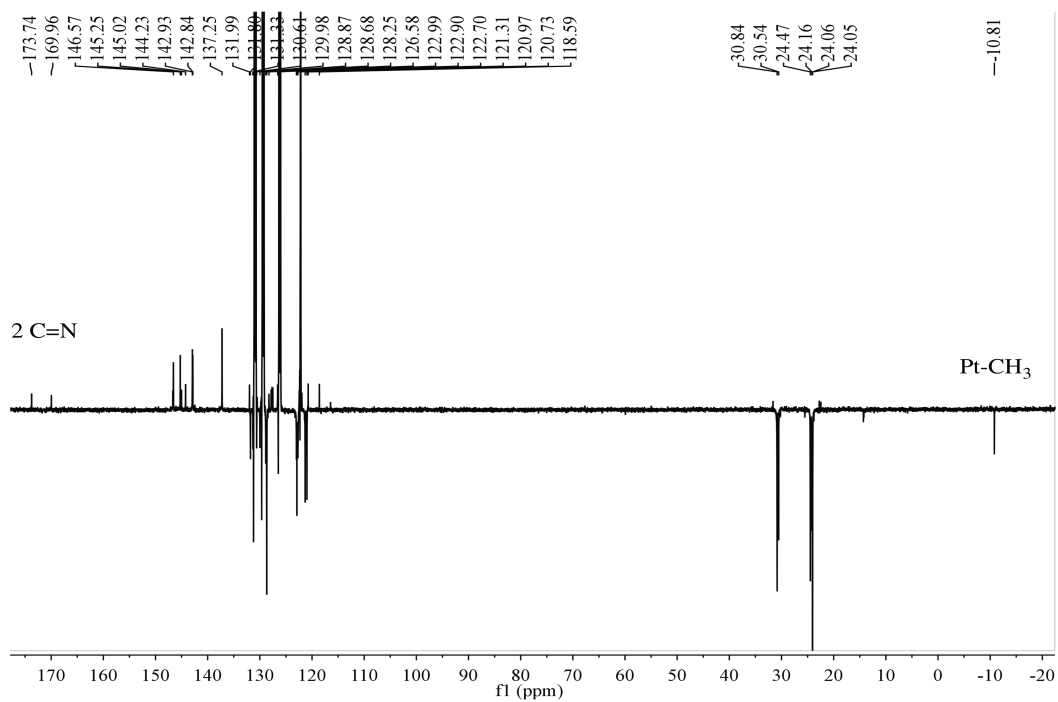


Figure S10. DEPT-Q ^{13}C NMR of **3-Ag** in $\text{C}_6\text{D}_5\text{Br}$ at 298K

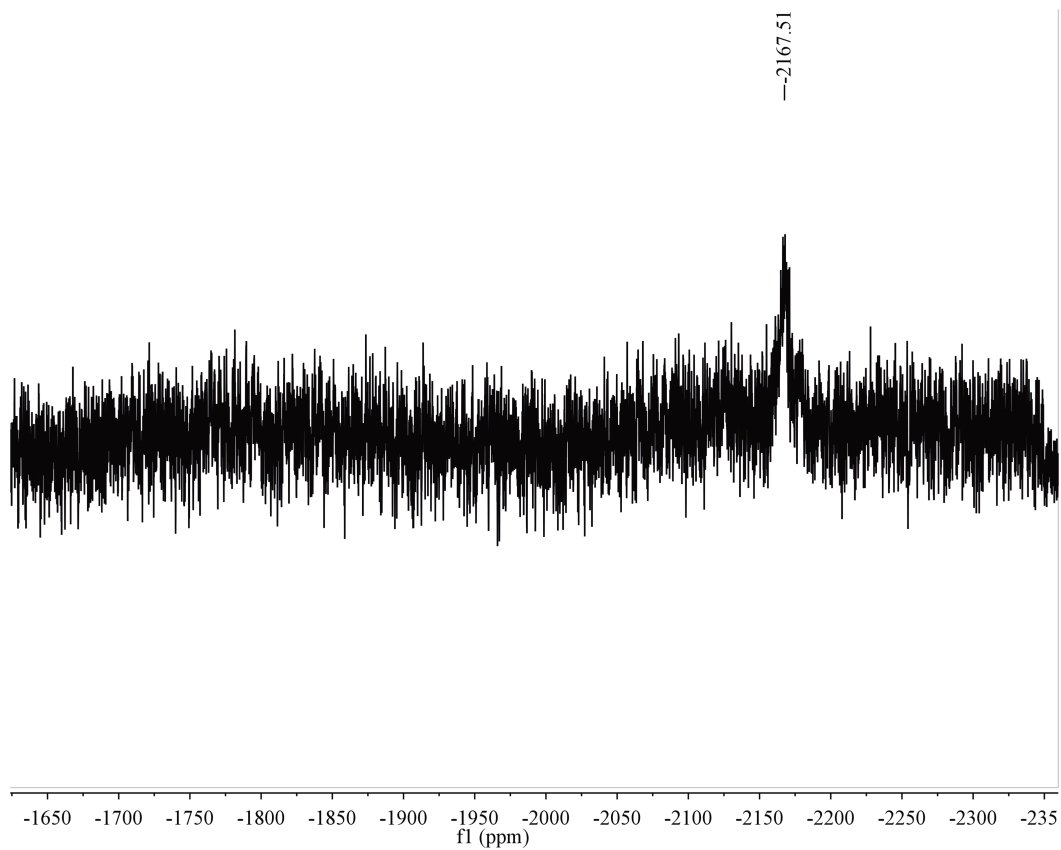


Figure S11. ^{195}Pt NMR of **3-Ag** in $\text{C}_6\text{D}_5\text{Br}$ at 298K

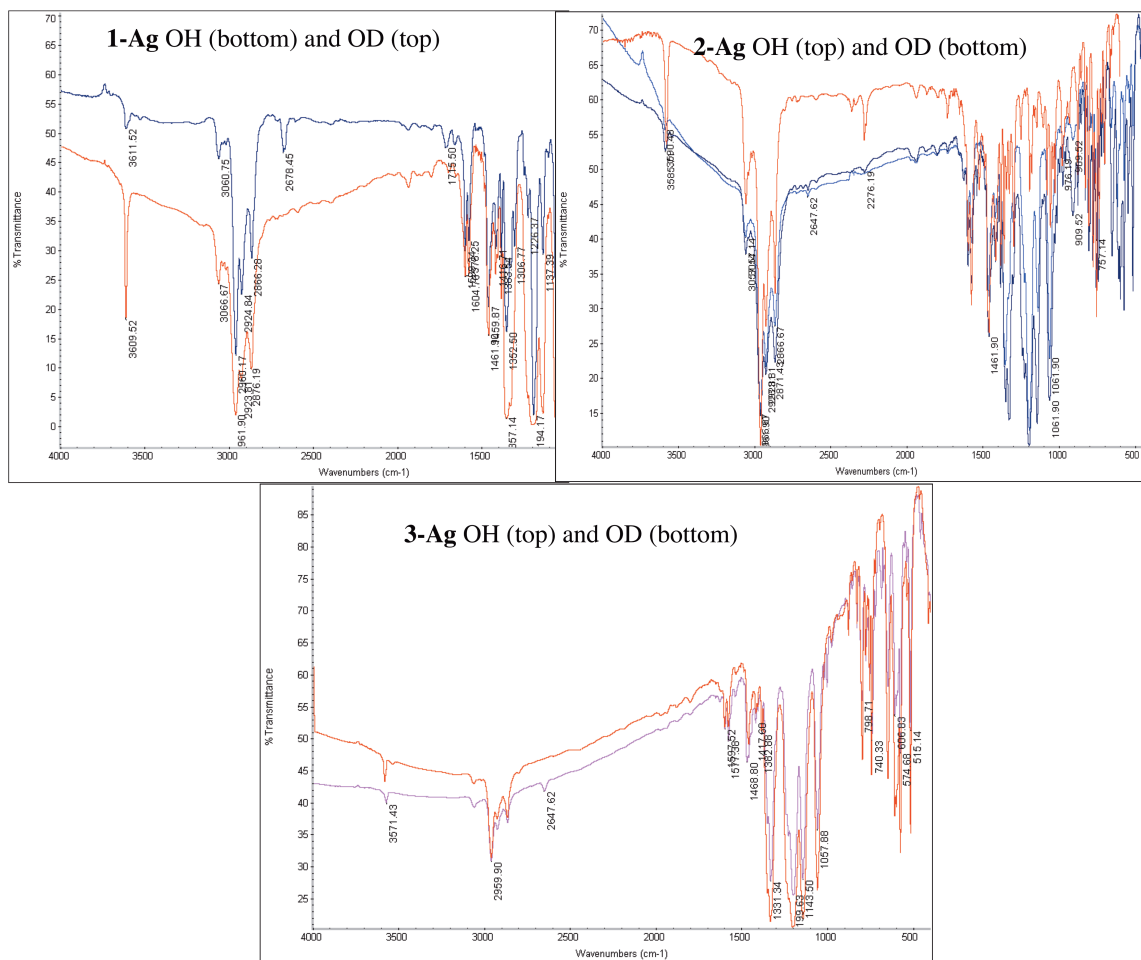


Figure S12. Stacked IR Spectra of OH and OD compounds of **1-Ag**, **2-Ag**, and **3-Ag**. The third spectra (also in blue) for **2-Ag** is a second attempt at the OD compound.

Table S1. Data collection and structure refinement details for **1-Ag**.

	1-Ag
formula	C ₉₆ H ₁₂₀ AgF ₆ N ₃ O ₁₄ PtS ₂
fw	4687.7
crystal system	Triclinic
space group	P-1
a, Å	12.6720(4)
b, Å	15.2570(5)
c, Å	26.7190(9)
α, deg	78.923(1)
β, deg	89.523(2)
γ, deg	67.966(1)
V, Å ³	4687.7(3)
Z	2
T, K	173
λ, Å	0.71073
ρ _{calc} , g/cm ³	1.346
F(000)	1942.0
μ, mm ⁻¹	1.808
Transmission Factors	0.760, 0.915
Data Completeness	0.912
Number of reflections	14687
θ max, deg	26.45
R ₁ (I > 2σ(I))	0.0698
wR ₂ (all data)	0.1857

References for Supporting Information:

1. Burger, B. J.; Bercaw, J. E., *Experimental Organometallic Chemistry*. American Chemical Society: Washington, D.C., 1987.
2. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996**, *15*, 1518-1520.
3. Lohr, T.L.; Piers, W.E.; Parvez, M. *Inorganic Chemistry*, **2012**, *51*, 4900-4902.
4. Lohr, T.L.; Piers, W.E.; Parvez, M. *Chemical Science*, **2013**, *4*, 770-775.
5. Lohr, T.L.; Piers, W.E.; Parvez, M. *Dalton Transactions*, **2013**, *42*, 14742-14748.